

Laser Separation of Oxygen Isotopes by IR Multiphoton Dissociation of $(\text{CH}_3)_2\text{O}$

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Abstract. Isotopically selective (with respect to ^{18}O) one- and two-frequency multiphoton dissociation of dimethyl ether $(\text{CH}_3)_2\text{O}$ by pulsed TEA CO_2 laser radiation has been studied. The maximum primary selectivity, $\alpha \cong 16$, is attained with the dissociation yields of the desired component $(\text{CH}_3)_2^{18}\text{O}$ $\beta_{18} = 5 \times 10^{-4}$ and 1.7×10^{-2} for one- and two-frequency excitation, respectively. The dependences of MPD yields and selectivity on laser radiation frequency, $(\text{CH}_3)_2\text{O}$ pressure, buffer gas (N_2) pressure and temperature have been measured. Multiphoton absorption coefficients have been measured and the average number of absorbed quanta calculated. The laser photon energy consumed for separating one ^{18}O atom has been estimated: 11 and ~ 4 keV/ ^{18}O atom for one- and two-frequency excitation, respectively.

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Various methods – IR multiphoton dissociation (MPD) of $(\text{CH}_3)_2\text{O}$, $(\text{CF}_3)_2\text{CO}$, COCl_2 and CF_3COF molecules [1–5], UV-dissociation of O_2 and H_2CO [6, 7], IR + UV excitation of OCS [8] – have been used in experiments on laser isotope separation (LIS) of oxygen¹. In most experiments the values of isotopic selectivity or separation factor for ^{18}O were found to be rather low – from 1.6 to 3.1 [1, 3–6, 8]. In UV photolysis of formaldehyde and its deuterium derivatives the selectivity was 8.9 for H_2CO , 17 for HDCO and 44 for D_2CO [7]. However, the natural concentration of HDCO and D_2CO is negligible, and the Cd laser used in [7] as a source of excitation does not look promising for technological purposes.

Except for high dissociation selectivity, practical realization of the LIS process poses some additional requirements. It is desirable, for example, that the starting substance should be a large scale product (or easily synthesized from such products) and the laser should offer an efficient and low cost source of radiation. Pulse repetition rate TEA CO_2 and excimer lasers seem to comply with these requirements today

[9, 10]. Therefore, when developing the process of oxygen LIS we chose the method of isotopically selective MPD of molecules by pulsed TEA CO_2 laser radiation.

The present work continues the search for a molecule to be used in industrial laser separation of oxygen isotopes. Earlier we studied isotopically selective MPD of $\text{CF}_3\text{CH}_2\text{OH}$ (2,2,2-trifluoroethanol) and $\text{C}_4\text{H}_8\text{O}$ (tetrahydrofuran) molecules [11]. In the case of $\text{CF}_3\text{CH}_2\text{OH}$ a selectivity for ^{18}O , $\alpha = 7.2$, was obtained. The goal of the present work is to investigate the isotopically selective MPD of the $(\text{CH}_3)_2\text{O}$ molecule (dimethyl ether) and to study the possibility of realizing the process of oxygen LIS using this molecule as a working substance.

The long-wave wing of the ν_{17} absorption band of $(\text{CH}_3)_2\text{O}$ with its centre at 1102 cm^{-1} [12] falls within the CO_2 laser turning range. The isotope shift for ^{18}O in the ν_{17} mode is 12 cm^{-1} [1]. The oxygen-selective dissociation of $(\text{CH}_3)_2\text{O}$ by pulsed TEA CO_2 laser radiation was the subject of investigation in [1, 2]. As ether was irradiated with a frequency of 1050.4 cm^{-1} , the $(\text{CH}_3)_2^{18}\text{O}$ molecules were selectively dissociated and CH_4 , C_2H_6 , CH_3OH , H_2CO , CO and H_2 were found as the dissociation products. The measured

¹ The natural abundance of oxygen isotopes is 99.759% for ^{16}O and 0.204% for ^{18}O

value of selectivity for ^{18}O was 1.7 [1]. As opposed to [1], where the laser radiation was strictly focused, the experiment carried out in [2] was performed with a near collinear laser beam and low fluence, from 1.6 to 2.4 J/cm 2 . The authors of that work claimed to achieve a selectivity value of $\alpha = 90$. This result will be discussed later in Sect. 3.

The possibility to achieve the high selectivity of MPD, the simple synthesis of $(\text{CH}_3)_2\text{O}$ from the available source (CH_3OH) , and the presence of a simple oxygen-containing molecule (CO) in the dissociation products – all this makes this compound rather interesting as far as practical realization of oxygen LIS is concerned.

1. Experiment

One- and two-frequency dissociation of $(\text{CH}_3)_2\text{O}$ with the natural abundance of oxygen isotopes was performed with two tunable TEA CO_2 lasers. The first laser used a $\text{CO}_2:\text{N}_2:\text{He}$ mixture with the ratio 1:0.15:4, the second one – with 1:0.37:4. Both radiation pulses had a peak with duration of 80 ns FWHM and a “tail” that contained less than one third of the total energy. The laser beams were collimated by a system of mirrors and NaCl lenses, with focal distance of 1.0 and 2.0 m. They were directed into a stainless steel cell, 12.2 cm long and 1.2 cm in inside diameter, with NaCl windows. For temperature measurements the cell used was made of stainless steel and had BaF_2 windows. Its length was 16.6 cm.

The cells were connected all the time with the MI 1309 mass-spectrometer input and evacuated to a pressure of 1×10^{-8} Torr.

The dissociation yields of $(\text{CH}_3)_2^{16}\text{O}$ (β_{16}) and $(\text{CH}_3)_2^{18}\text{O}$ (β_{18}) were determined from the mass spectra of irradiated and unirradiated ether. For this purpose argon was added as a reference mark into the gas in the ratio $(\text{CH}_3)_2\text{O}:\text{Ar} = 10:1$. The decomposition of both components was determined as the ratio $A_{16} = \frac{(I_{46}/I_{40})_N}{(I_{46}/I_{40})_0}$ or $A_{18} = \frac{(I_{48}/I_{40})_N}{(I_{48}/I_{40})_0}$ for ^{16}O and ^{18}O , where I_{46} , I_{48} , I_{40} are the peak intensities with $m/e = 46, 48$ and 40 which correspond to the molecular peaks of $(\text{CH}_3)_2^{16}\text{O}^+$, $(\text{CH}_3)_2^{18}\text{O}^+$ and Ar^+ measured in the irradiated (index “N”) and unirradiated (index “0”) samples.

The values of dissociation yield β_{16} , β_{18} and selectivity α were found using the following relations

$$\beta_{16} = \frac{1}{\Gamma} [1 - N\sqrt{A_{16}}], \quad \beta_{18} = \frac{1}{\Gamma} [1 - N\sqrt{A_{18}}]$$

$$\alpha = \beta_{18}/\beta_{16},$$

where N is the number of laser pulses, Γ is the ratio of the irradiated volume to the cell volume.

IR spectra of dimethyl ether at pressures of 1, 10, and 100 Torr were measured before the experiments. There was a good agreement of the frequencies with those from [12] and to within an accuracy of $\sim 10^{-2}$ the spectrum contained no unidentified bands.

2. Results

The experiments on isotopically selective single-frequency MPD (except for spectral measurements) were performed at the laser radiation frequency $\omega_{\text{las}} = 1050.4 \text{ cm}^{-1}$ (the 9P16 line of CO_2 laser) with the energy fluence $\phi = 3.8 \pm 0.2 \text{ J/cm}^2$. The dissociation yields of the both isotopic components $(\text{CH}_3)_2^{16}\text{O}$ and $(\text{CH}_3)_2^{18}\text{O}$ and selectivity, were determined as functions of the laser radiation frequency, the $(\text{CH}_3)_2\text{O}$ pressure, the buffer gas (nitrogen) pressure and temperature. Such measurements including two-frequency experiments enable one not only to optimize the parameters of an initial photochemical act of separation but also to study the very process of multiphoton (MP) excitation and dissociation of polyatomic molecules [9, 13–16].

Figure 1 illustrates MPD yields (β_{18} and β_{16}) and selectivity (α) as functions of laser radiation frequency ω_{las} . The same figure shows a linear absorption spectrum for the ν_{17} band. In the frequency range concerned, the dissociation yields drop at different rates as the frequency decreases and the selectivity increases and reaches 10 at 1039.4 cm^{-1} (the 9P28 line of CO_2 laser).

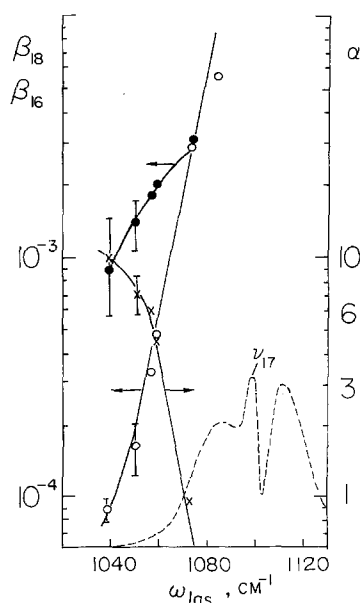


Fig. 1. MPD yields of $(\text{CH}_3)_2^{16}\text{O}$ (β_{16}) and $(\text{CH}_3)_2^{18}\text{O}$ (β_{18}) molecules and isotopic selectivity $\alpha = \beta_{18}/\beta_{16}$ as functions of laser radiation frequency ω_{las} . $\phi = 2.6 \pm 0.2 \text{ J/cm}^2$. β_{18} (—●—), β_{16} (—○—), α (—×—)

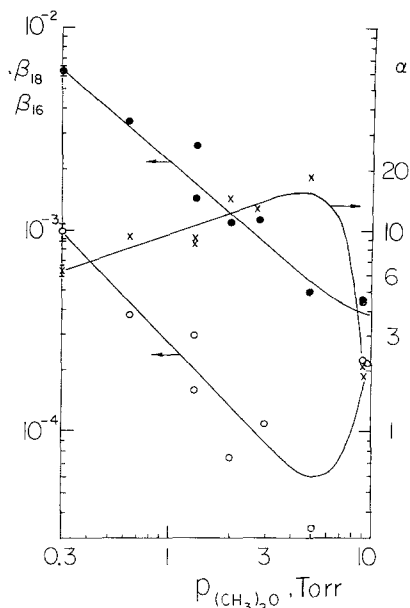


Fig. 2. MPD yields β_{18} and β_{16} and selectivity α versus $(\text{CH}_3)_2\text{O}$ pressure. $\omega_{\text{las}} = 1050.4 \text{ cm}^{-1}$, $\phi = 3.8 \pm 0.2 \text{ J/cm}^2$

The influence of collisions on the dissociation yields and selectivity at increasing pressures of $(\text{CH}_3)_2\text{O}$ or the buffer gas was studied in subsequent experiments. Figure 2 shows the dependences of β_{18} and β_{16} and α on the $(\text{CH}_3)_2\text{O}$ pressure. An increase in ether pressure decreases β_{18} and β_{16} . In this case within the measurement error β_{16} falls off inversely with pressure, while β_{18} decreases more slowly, with the result that the MPD selectivity grows from 6.3 at 0.3 Torr to 16 at 5 Torr. A further increase in pressure brings about a drastic growth of the dissociation yield of molecules of the undesired isotope $(\text{CH}_3)_2^{16}\text{O}$ leading to rapid loss of MPD selectivity.

Figure 3 shows the dependences of yields and selectivity on the pressure of nitrogen, the buffer gas. An increase in N_2 pressure causes both β_{18} and β_{16} to decrease starting from the very low pressures of N_2 . In this case β_{18} drops faster, with the result that the dissociation selectivity decreases. The figure also presents the values of β_{18} , β_{16} and α with a lighter buffer gas (D_2) added. It may be seen that deuterium causes a faster decrease of dissociation yields.

For many compounds a decrease in gas temperature is known to increase MPD selectivity, sometimes considerably [9]. So we had to measure temperature dependences of dissociation yields and selectivity. The dependences obtained are typical enough (see Fig. 4). As the temperature decreases (from $+67^\circ\text{C}$ to -46°C), β_{18} and β_{16} are reduced by 6.6 and 12 times respectively and α grows from 4.7 to 8.6.

Thus, in case of one-frequency excitation the highest dissociation selectivity (at room temperature)

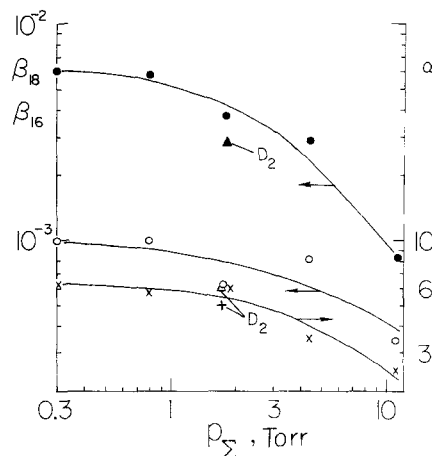


Fig. 3. Dependence of β_{18} , β_{16} and α on total pressure of $(\text{CH}_3)_2\text{O}$ and N_2 (P_Σ). $(\text{CH}_3)_2\text{O}$ pressure — 0.3 Torr, ω_{las} and ϕ are the same as in Fig. 2. The symbols \blacktriangle , \triangle , $+$ correspond to β_{18} , β_{16} , α in the case where 1.5 Torr D_2 is added

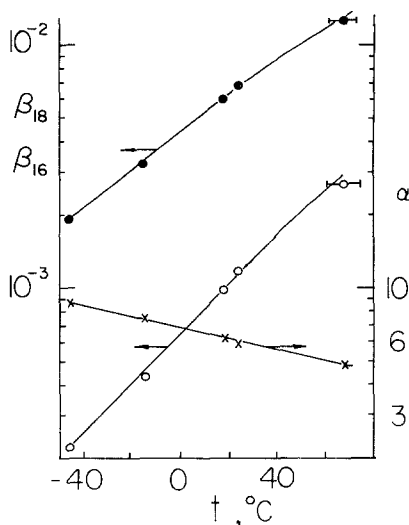


Fig. 4. Dependence β_{18} , β_{16} and α on gas temperature t . $(\text{CH}_3)_2\text{O}$ pressure — 0.3 Torr. ω_{las} and ϕ are the same as in Fig. 2

$\alpha = 16$ is achieved as $(\text{CH}_3)_2\text{O}$ at a pressure of 5 Torr is irradiated by laser radiation with $\omega_{\text{las}} = 1050.4 \text{ cm}^{-1}$ and $\phi \cong 3.8 \text{ J/cm}^2$. But the dissociation yield of the desired component $(\text{CH}_3)_2^{18}\text{O}$ under such conditions is very low, $\beta_{18} = 5 \times 10^{-4}$. To increase the parameters of an initial photochemical separation act we used two-frequency excitation. Table 1 presents the results of a search for an optimal combination of frequencies and fluences of the first and second laser fields.

It can be seen that the selectivity and β_{18} values are determined mainly by the fluence value of the first field and the frequency shift of the both fields from the center of ν_{17} linear absorption band. Note that, even when the fluence is lower than that of one-frequency excitation, the MPD yield β_{18} can be increased by about

Table 1. Dependence of $(\text{CH}_3)_2\text{O}$ dissociation yields (β_{16} and β_{18}) and selectivity (α) on frequency and fluence of two laser fields. $(\text{CH}_3)_2\text{O}$ pressure is 0.3 Torr. Laser pulse delay is 300 ± 50 ns

Laser lines	J/cm ²	$\beta_{18} \times 10^2$	$\beta_{16} \times 10^3$	$\alpha = \beta_{18}/\beta_{16}$
9R10+9P26	1.3+1.6	1.2	3.2	3.7
9R10+9P26	1.1+1.9	0.81	1.2	6.8
9R10+9P36	1.0+2.0	1.3	1.4	9.6
9R10+9P36	0.6+1.6	0.25	0.76	3.3
9R10+9P36	1.1+2.3	1.7	2.0	8.3 ^a
9P6+9P36	1.0+1.9	0.45	0.54	8.3 ^a
9P6+9P36	1.1+2.0	1.6	1.1	13.2

^a Laser mixture for the first field 1:1:4

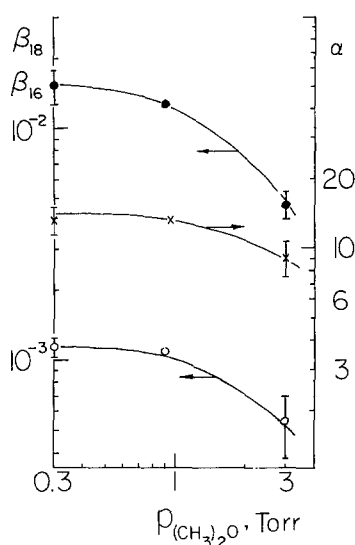


Fig. 5. MPD yields β_{18} and β_{16} and selectivity α as a function of $(\text{CH}_3)_2\text{O}$ pressure for two-frequency excitation. Laser radiation parameters – $\omega_1 = 1058.9 \text{ cm}^{-1}$, $\omega_2 = 1031.5 \text{ cm}^{-1}$, $\phi_1 = 1.1 \text{ J/cm}^2$, $\phi_2 = 2.2 \text{ J/cm}^2$. Second pulse delay is 300 ± 50 ns

3 times. The subsequent experiments on two-frequency MPD under collisional conditions were performed with the following laser frequencies and fluences: $\omega_1 = 1058.9 \text{ cm}^{-1}$ (9P6), $\omega_2 = 1031.5 \text{ cm}^{-1}$ (9P36); $\phi_1 = 1.1 \text{ J/cm}^2$, $\phi_2 = 2.2 \text{ J/cm}^2$.

An increase in $(\text{CH}_3)_2\text{O}$ pressure leads to decreased yields of two-frequency MPD β_{18} and β_{16} (see Fig. 5). Since β_{18} decrease more rapidly than β_{16} the selectivity drops from 13 at 0.3 Torr to 9 at 3 Torr.

Two-frequency excitation gives a pronounced advantage compared with one-frequency excitation. The same selectivity $\alpha = 10$, for example, can be attained with a simultaneous increase of the MPD yield β_{18} from 1.8×10^{-3} to 6×10^{-3} and the ether pressure from 1.3 to 2.5 Torr.

Figure 6 illustrates the two-frequency MPD yields and selectivity as functions of N_2 pressure. Compared

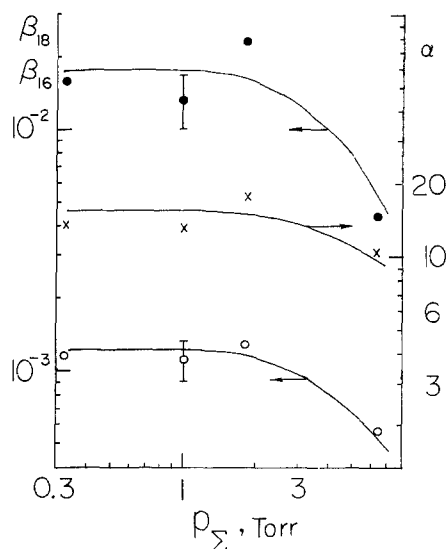


Fig. 6. β_{18} , β_{16} , α versus the total pressure of $(\text{CH}_3)_2\text{O}$ and N_2 (P_Σ) for two-frequency excitation. $(\text{CH}_3)_2\text{O}$ pressure 0.3 Torr. The other parameters are as in Fig. 5

to the analogous dependences for one-frequency MPD (Fig. 3), the values of β_{18} , β_{16} and α are constant up to an N_2 pressure of 2 Torr. A further increase in N_2 pressure causes the MPD yields and selectivity to drop.

To evaluate the laser energy consumption for separation of one atom of the rare isotope ^{18}O , one of the most important characteristics of the separation process, we measured the multiphoton absorption coefficients k of $(\text{CH}_3)_2\text{O}$ excitation with $\omega_{\text{las}} = 1050.4 \text{ cm}^{-1}$ (9P16) and determined from them the average number of quanta \bar{n} absorbed by one molecule of the gas. The values of k and \bar{n} at various ether pressures are given in Table 2. Note that an increase in pressure brings about a moderate rise in the average excitation level of \bar{n} that, with $P(\text{CH}_3)_2\text{O} = 1$ Torr, is equal to about 1 quantum/molecule.

Table 2. MP absorption coefficients k and the average number of absorbed quanta \bar{n} (per molecule) at different $(\text{CH}_3)_2\text{O}$ pressures. $\omega_{\text{las}} = 1050.4 \text{ cm}^{-1}$ (9P16), $\phi = 3.8 \pm 0.2 \text{ J/cm}^2$

$P(\text{CH}_3)_2\text{O}$ [Torr]	k [m^{-1}]	\bar{n} [quanta/molecule]
2.7	0.08 ± 0.06	1.5 ± 1.2
9.1	0.19 ± 0.06	1.1 ± 0.4
27	0.78 ± 0.06	1.5 ± 0.1

We tried using mass spectrometry to find oxygen-containing products to measure the ^{18}O enrichment factor in MPD products. But at low decompositions of the initial material $(\text{CH}_3)_2^{16}\text{O}$ ($\leq 10\%$) only methane and ethane were recorded. At high decompositions (about one half the molecules of the rich isotope) the peaks of CO and CH_3OH (with less reliability) were recorded in the mass spectra, but their intensity did not comply with the number of dissociated molecules. As for CH_3OH , this could be related to its adsorption on the walls of the cell of the mass spectrometer input. It was impossible to find formaldehyde among the dissociation products. This may be explained by H_2CO adsorption on the walls as well as by the fact that it is difficult to record its peaks against the background of the peaks of residual $(\text{CH}_3)_2\text{O}$ and newly-formed C_2H_6 .

Using absolute calibration of the mass spectrometer against CO we could estimate the relative yield of CO^2 that was $\sim 6 \times 10^{-2}$.

3. Discussion of Results

Here we shall first consider chemical reactions giving rise to final products and their influence on the primary parameters of MPD.

A sequence of chemical reactions after the primary act of photodissociation was suggested in [1, 2] to explain the set of final products observed. According to [1], the set of products resulting from IR MPD and pyrolysis of dimethyl ether [17] is the same. This is quite possible because in [1] strong focusing of laser radiation was used and, hence, a high vibrational temperature and a high initial concentration of the primary CH_3 and CH_3O radicals were obtained in the waist. Besides, to explain the observed set of products it is assumed in [1] that under the conditions of the experiment reactions may take place between the formed radicals and dimethyl ether itself.

In our opinion, under the conditions of our experiment final dissociation products are formed without $(\text{CH}_3)_2\text{O}$ involved. The estimation of reaction rates

from known constants [18] with due regard for radical concentration ($\sim 10^{-3}$) shows that the rates of reactions between the radicals are at least about 3 orders higher than those of reactions between the radicals and $(\text{CH}_3)_2\text{O}$.

Thus, it may be considered that the MPD yields and selectivity observed in our experiments are not affected by the subsequent reactions of radicals (except for a possible reaction of recombination).

As for the presence of CO among the dissociation products at a low laser radiation fluence ($2\text{--}4 \text{ J/cm}^2$), this seems to be caused by the following factors. Reactions between the CH_3 and CH_3O radicals producing CH_4 , C_2H_6 , CH_3OH , H_2CO , and $(\text{CH}_3)_2\text{O}$ have the highest rates, $\sim (1\text{--}10) 10^{13} \text{ cm}^3/\text{mol} \cdot \text{s}$ [18]. Carbonic oxide, we assume may be formed as CH_3O acts on the formaldehyde accumulated in the cell, the concentration of which is comparable to the value of decomposed $(\text{CH}_3)_2\text{O}$ and can be as high as $\sim 10^{-1}$. The estimation of reaction rates with due regard for the CH_3O concentration ($\sim 10^{-3}$) shows that CO may be formed with a concentration 10^{-2} relative to the other dissociation products. This value agrees well with the experimental value of CO yield $\sim 6 \times 10^{-2}$. The isotopic ratio in CO, as it is formed by such chemical reactions, should comply with the selectivity of the primary act of photodissociation.

It should be noted however that small amounts of a dissociation product such as C_2H_6 can introduce large errors into isotopic analysis of CO (increasing the ^{18}O enrichment factor calculated from the peaks with $m/e = 28$ and 30). The point is that the mass peak produced by the molecular ion C_2H_6^+ with $m/e = 30$ is superimposed on the peak of $^{12}\text{C}^{18}\text{O}^+$. The presence of C_2H_6 traces in CO after the latter is distilled from MPD products and $(\text{CH}_3)_2\text{O}$ is most likely connected with the residual C_2H_6 pressure at the distillation temperature, even though this pressure is low. Usually it is at the temperature of liquid or solid nitrogen (in [2], for example). The error increases in the case of small quantities of CO, that is, at low decomposition of the initial species. In our experiment, after 50% decomposition of $(\text{CH}_3)_2\text{O}$ in oxygen-containing dissociation products, a 1.7-fold (as calculated from measured yields of $(\text{CH}_3)_2^{18}\text{O}$ and $(\text{CH}_3)_2^{16}\text{O}$ species) enrichment with ^{18}O should have been observed. But the enrichment factor measured from the peaks with $m/e = 28$ and 30 was about 6; this points to a considerable contribution of C_2H_6 to the peak with $m/e = 30$. In this experiment CO was separated from the other products and from $(\text{CH}_3)_2\text{O}$ by freezing the latter for 10 min at liquid nitrogen temperature. Nevertheless, the C_2H_6 pressure that corresponds to 77 K ($\sim 4 \times 10^{-4}$ Torr) is quite enough to introduce an error into the isotopic analysis of CO.

² The relative yield of CO is defined as the number of CO molecules formed by the dissociation of one $(\text{CH}_3)_2\text{O}$ molecule

Thus it is seen that the effect of C_2H_6 may be very important. A high value of selectivity $\alpha = 90$ was found in [2] from the isotopic analysis of CO. Our measurements of selectivity from decomposition of $(CH_3)_2^{16}O$ and $(CH_3)_2^{18}O$, give a somewhat lower value of α as in [1]. Taking into account the above discussion we believe that the α values measured in [2] are overestimated due to the interference of CO and C_2H_6 mass peaks.

The results of one-frequency MPD of $(CH_3)_2O$ given in Figs. 2–4 can be explained in the same way as in [13, 15, 16] for some freons. In particular, it was shown in experiments with CF_3Br [15], that in typical conditions of laser isotope separation (long-wave detuning from linear absorption bands of both isotopes) the molecules are excited from rather narrow zones of thermally populated initial vibrational states. The average energy of these states may be considerably higher compared with the thermal vibrational energy. Using the technique developed in [15] one can estimate the average starting energies for both $(CH_3)_2^{16}O$ and $(CH_3)_2^{18}O$ molecules. When excited at 1050.4 cm^{-1} $(CH_3)_2^{16}O$ molecules start from vibrational states with an average energy of $\approx 1460\text{ cm}^{-1}$. The estimated width of related zones must be less than 100 cm^{-1} to account for the measured yield values. For $(CH_3)_2^{18}O$ molecules the starting energy is $\approx 1200\text{ cm}^{-1}$. The results of [15] enable us to conclude that small values of dissociation yields may be explained by rather a high position of starting vibrational states, and a small difference in vibrational energies of these states for various isotopic components is responsible for the low MPD selectivity.

The specific feature of $(CH_3)_2O$ MPD is that there is not a characteristic part of initial growth in the buffer gas pressure dependence of dissociation yield (Fig. 3) that is usually associated with the rotational ‘bottle neck’ effect [9]. The lack of growth in yields cannot be explained by the ‘sticking’ of molecules below the onset of the quasi-continuum, due to the field ‘bottle neck’ [14] because upon two-frequency excitation with a buffer gas added, no growth in MPD yields is observed either. Such behaviour of β_{18} and β_{16} as functions of N_2 pressure may be conditioned by the following factors. The most probable one, we think, is caused by a higher rate of rotational relaxation compared with the rate of laser excitation of molecules from resonant rotational sublevels [13]. But taking into account a large laser frequency ($\sim 50\text{ cm}^{-1}$) from the center of linear absorption band we cannot exclude the possibility that the molecules from different rotational states interact with the laser radiation more or less uniformly and that there is no hole burning in the rotational distribution as found for large detuning in SF_6 [19].

The dependences of MPD yields and selectivity on $(CH_3)_2O$ pressure are rather typical and have been already observed for other molecules [9, 16, 20, 21]. Since it may be assumed that the laser radiation interacts with only a small part of molecules thermally excited to high-lying vibrational states with average energies of 1200 and 1460 cm^{-1} , the MPD excitation of $(CH_3)_2O$ is probably characterized by the vibrational ‘bottle neck’ effect. Its action is described in detail in [16]. It should be clarified that, as the $(CH_3)_2O$ pressure increases, the MPD yields decrease due to deactivation of a small fraction of highly excited molecules by V–V exchange with the bath of vibrationally low excited molecules of the rich isotope $(CH_3)_2^{16}O$ for the most part. The drastic growth in $(CH_3)_2^{16}O$ dissociation yield at a certain pressure excess is determined by self-accelerating vibrational ‘heating’ of these molecules.

Some words about the efficiency of $(CH_3)_2O$ two-frequency excitation: When the total laser radiation fluence is even lower than that in case of one-frequency excitation, the dissociation yield of $(CH_3)_2^{18}O$ molecules increases by about three times. It is mainly due to this that the corresponding selectivity increases by three times. The frequencies of the first and second fields ($\omega_1 = 1058.9\text{ cm}^{-1}$ and $\omega_2 = 1031.5\text{ cm}^{-1}$) seem to be not quite optimal for exciting $(CH_3)_2^{18}O$ molecules. This is confirmed by the dependences of β_{18} and β_{16} on $(CH_3)_2O$ or N_2 pressures (see Figs. 5 and 6). Indeed, at increasing pressure β_{18} drops faster than β_{16} which points to a stronger influence of V–V or V–T deactivation on the process of MP excitation of $(CH_3)_2^{18}O$. The latter is possible at a lower rate of laser excitation of these molecules. It can be seen from Table 1 that the long-wave detuning of the both radiation frequencies from the center of the linear absorption band causes increased MPD yields of $(CH_3)_2^{18}O$ mainly. The dissociation yields of $(CH_3)_2^{16}O$ in this case change slightly. Further optimization of two-frequency excitation at least for the second field, however, is limited by the CO_2 laser turning range.

As for process of oxygen isotopes separation on the basis IR MPD, dimethyl ether has got some advantages over the molecules investigated before. Firstly, a sufficiently high value of the MPD selectivity of the ^{18}O isotope $\alpha \approx 16$ was attained in this work. The dissociation yield of the desired component in this case ranges from 5×10^{-4} to 1.7×10^{-2} . These parameters have been obtained at a comparatively low laser radiation fluence, from 3.3 to 3.8 J/cm^2 . Secondly, $(CH_3)_2O$ can be easily synthesized from (CH_3OH) , an abundant raw material.

The photon energy consumed for separating one ^{18}O atom is rather high. At low pressures of dimethyl

ether (0.3 Torr) it is 11 keV/ ^{18}O atom for one-frequency excitation and ~ 4 keV/ ^{18}O atom for two-frequency excitation³. An increase in $(\text{CH}_3)_2\text{O}$ pressure leads to higher energy consumption due to a decrease in dissociation yield of the desired component $(\text{CH}_3)_2^{18}\text{O}$. For example, $\alpha = 10$ can be achieved in the case of one-frequency MPD with a $(\text{CH}_3)_2\text{O}$ pressure of 1.3 Torr, and in the case of two-frequency MPD at 2.5 Torr. The energy consumed increases in this case to 36 and ~ 11 keV/ ^{18}O atom, respectively.

It should be said that the compound studied by us as a starting substance for the technological process has its own shortcomings. First of all, one obtains small dissociation yields of the desired component $(\text{CH}_3)_2^{18}\text{O}$ which do not exceed 1.7×10^{-2} even at two-frequency excitation. This value can be attained only with the use of low-nitrogen laser mixture and, hence, with a small efficiency of the CO_2 laser. Besides, the basic oxygen-containing dissociation products are methanol and formaldehyde. It is very difficult to separate the latter from $(\text{CH}_3)_2\text{O}$ since H_2CO and $(\text{CH}_3)_2\text{O}$ have similar saturated vapor pressures at the same temperature and probably some chemical methods should be used. Another possible way of eliminating this shortcoming and producing only one oxygen-containing product is to introduce scavengers of oxygen-containing radical CH_3O .

4. Conclusions

1. Isotopically selective (with respect to ^{18}O) multiphoton dissociation of dimethyl ether $(\text{CH}_3)_2\text{O}$ by one- and two-frequency CO_2 laser radiation has been investigated. The maximum primary selectivity, $\alpha \cong 16$, is attained with dissociation yields of the desired component $(\text{CH}_3)_2^{18}\text{O}$ $\beta_{18} = 5 \times 10^{-4}$ and $\beta_{18} = 1.7 \times 10^{-2}$ in case of one- and two-frequency excitation.

2. The obtained dependences of one-frequency MPD yields and selectivity on temperature and $(\text{CH}_3)_2\text{O}$ pressure can be interpreted in the framework of the mechanisms developed before in [15, 16].

3. Multiphoton absorption coefficients in dimethyl ether have been measured and the average absorbed energy (~ 1 quantum/molecule) estimated from them. This has allowed an estimation of the laser photon energy consumed for separating one ^{18}O atom. For one-frequency MPD it is 11 keV/ ^{18}O atom and for two-frequency MPD it is ~ 4 keV/ ^{18}O atom.

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³ The last estimation assumes that the sum of average energies absorbed from each field is ~ 1 quantum/molecule, as in one-frequency dissociation